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FREQUENCY RESPONSE OF ELECTROCHEMICAL CELLS

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INTRODUCTION

Electrochemical processes may and have been studied using frequency response techniques and modeled using impedance concepts. Processes that occur at electrodes may be modeled as resistance, capacitance or complex impedance. More information may be gained using dynamic techniques than by using steady-state D.C. techniques. For example, one could study an electrode by measuring steady D.C. current and potential, or the same system could be studied using A.C. over a range of frequencies with an increase in the amount of information learned. Dynamic techniques have been used to estimate the specific area of porous lead-acid battery electrodes (Newman and Tiedemann, 1976), the kinetics and mechanisms of electrode reactions and the rate of mass-transport processes such as diffusion (Bard and Faulkner, 1980). Attempts have been made to correlate cell state of charge with A.C. impedance spectra (Brodd and DeWane, 1963; Sathyanarayana et al., 1979). Zimmerman et al. (1982) studied the very low frequency impedance (as low as 0.1 Hz) of NiCd cells.

OBJECTIVES

The objective of this work was to examine the feasibility of using frequency response techniques 1) as a tool in destructive physical analysis of batteries, particularly for estimating electrode structural parameters such as specific area, porosity and tortuosity and 2) as a non-destructive testing technique for obtaining information such as state of charge and acceptability for space flight. It would be desirable to have a non-destructive battery test that can be run rapidly and as close to launch of spacecraft as possible. The battery frequency response may be such a test.

THEORY

The phenomena that contribute to the frequency response of an electrode include 1) double layer capacitance, 2) Faradaic reaction resistance, 3) mass transfer or Warburg impedance and 4) ohmic solution resistance. The double layer is a thin (about 20 Angstrom) layer of electric charge that exists at the boundary between two phases, such as an electrode/solution interface, and can be formed by preferential absorption of an ion on the surface or by orientation of polar solvent molecules. Double layers are also formed when a potential difference is placed across a cell. For example, if the applied potential is less than the decomposition potentials of the electrolyte or solvent then no steady state current can flow in the cell and there is no ohmic potential gradient. The applied potential difference occurs across the double layer. The double layer can be considered as an electric capacitor since it acts to store charge. The concept of the double layer was experimentally verified with mercury which has the advantage of a reproducible liquid surface and of inhibiting hydrogen evolution (Newman, 1973). The double layer capacitance is on the order of $10 \mu\text{F}/\text{cm}^2$, which corresponds to a parallel plate capacitor with a plate separation of about 20 Å, the double layer thickness. The double layer capacitance is potential dependent, but can be treated as constant over small (7 mV) potential range.

The Faradaic reaction resistance models chemical reaction rate at the electrode surface (current density) as a function of potential difference across the double layer. This resistance is highly non-linear, but can be linearized for potential perturbations of about 5 mV. Most electrodes used in practical energy systems exhibit combined chemical reaction and double

layer charging. For a bare metal electrode in contact with solution this can be modeled as a parallel RC circuit.

Slow diffusion of reactants to the electrode surface or of reaction products away from the surface also causes the potential to lag the current. This impedance component is called Warburg impedance. For a planar electrode in a large excess of electrolyte solution a pure Warburg impedance causes a phase shift of 45 degrees that is independent of frequency. The Warburg impedance is usually manifested at frequencies less than 1 Hz. Measurements at frequencies as low as 0.0001 Hz have been reported. The period of such a measurement is about as long as a battery cycle, however the state of charge would probably not be altered significantly since the voltage and current amplitudes are small.

Finally, the ohmic resistance of the bulk electrolyte solution needs to be considered. Figure 1 shows a simple equivalent circuit for a planar electrode that includes all of the phenomena discussed.

Most actual battery electrodes are high surface area porous electrodes, with the electrode processes are distributed throughout the electrode volume instead of at a single surface. One porous electrode model is the idealized cylindrical pore. The pore walls are the solid surface where the electrode reaction and double layer charging occurs. At the electrode grid all of the current is in the solid phase while at the electrode/separator boundary all of the current is in the liquid phase. The current is transferred from the liquid to the solid along the pore wall.

Figure 2 shows a model circuit for the pore, which is often called a transmission line model. The impedance Z can include reaction, double layer capacitance and Warburg impedance. The impedance of the electrode, assuming a very large solid conductivity, is

$$Z_{\text{pore}} = \frac{a}{km^2} \frac{\sinh(mL) + \frac{a}{m} \cosh(mL)}{\left[\frac{1}{\epsilon} \left(\frac{a}{m} \right)^2 + (1 - \epsilon) \right] \sinh(mL) + \frac{a}{m} \cosh(mL)}$$

where

$$m^2 = R_f^{-1} + j\omega C \quad \begin{array}{l} \text{Warburg impedance neglected} \\ L = \text{electrode thickness} \end{array}$$

This is a rather complicated expression that includes hyperbolic functions of complex numbers. The method of non-linear least squares (Boukamp, 1986) can be used to fit experimental data to the expression and find the best values of the specific surface area a , the porosity ϵ , and the double layer capacitance and reaction resistance.

EXPERIMENTAL

Nickel-cadmium cells were constructed using electrodes from unused Eagle-Picher 50 A-Hr cells that had undergone destructive physical analysis. A negative and positive electrode were placed in a plexiglass container. No separator was used, but an electrode spacing of 1 cm was maintained using plexiglass ribs. Nitrogen flowed continuously in the cell to prevent contamination by carbon dioxide. A Ag/AgO reference electrode was placed in a separate compartment with electrolyte. The two compartments were connected by a 1 mm Teflon tube filled with electrolyte. Electrolyte concentrations tested were 1% and 31% KOH.

A EG&G/PAR model 363 potentiostat was used to control the potential between the Cd and reference electrode. A Wavetek signal generator supplied the voltage perturbations that were added to the D.C. offset voltage of the potentiostat. The potential and current monitors of the potentiostat were connected to a Tektronics storage oscilloscope, from which the peak current, peak voltage and phase angles were obtained.

ACCOMPLISHMENTS

A significant amount of data for Ni and Cd electrodes in 31% and 1% KOH has been acquired. Quantitative data analysis will be performed during the coming months. Some initial observations are : 1) use of the 1% KOH seems useful for DPA since it results in phase lag at lower frequencies than for the 31% KOH. 2) Phase lags of greater than 90 degrees were observed at high frequency. One possible explanation for this is that dielectric polarization of one of the electrode materials becomes significant at high frequency.

A paper has been accepted for presentation at the Fall 1990 Electrochemical Society Meeting, and a second paper is being prepared for the Spring 1991 meeting.

FUTURE WORK

This summers effort has been concentrated on data acquisition. Quantitative data analysis, using the software developed this summer, will be performed in the coming months.

This effort will continue for at least one more year with the support of the Center Directors Discretionary Fund. State of the art equipment is being procured under that support that will enable data to be acquired with increased accuracy and rapidity. Future efforts will include 1) application of these techniques to nickel-hydrogen and silver-zinc batteries and 2) study of failed cells and development of non-destructive testing techniques. At least one graduate student will be involved in future research work.

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FIGURES

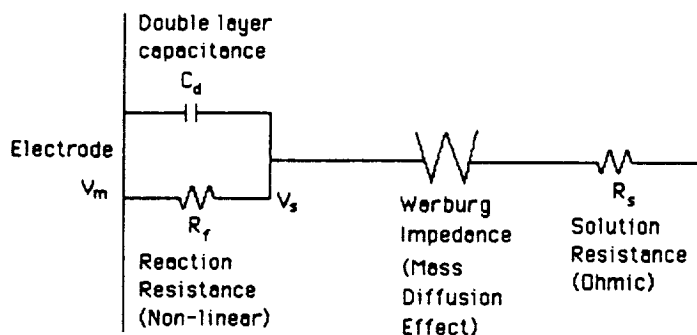


Figure 1. Equivalent circuit representing processes at a planar electrode.

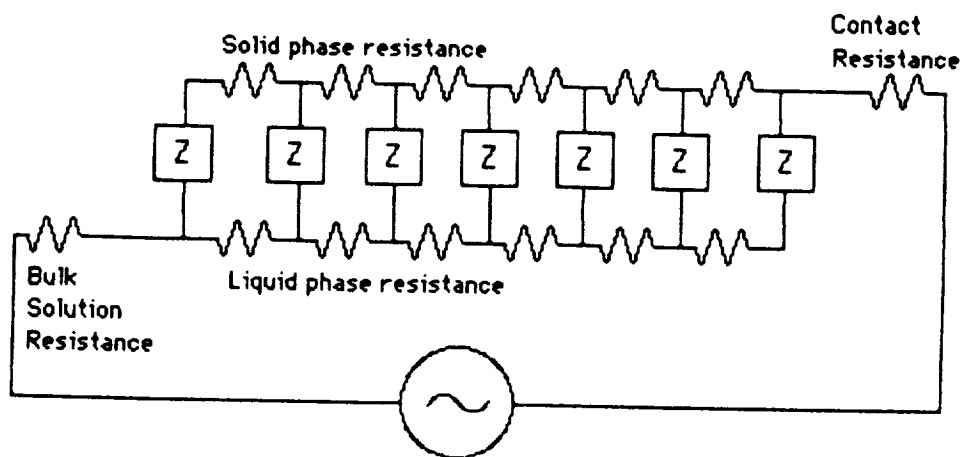


Figure 2. Equivalent circuit representing processes in an idealized pore.